Europäisches Patentamt
European Patent Offic
Office européen d s brevets

⑲ ⑪ Publication number: 0 318 295 A1

EUROPEAN PATENT APPLICATION

㉑ Application number: 88311148.6

㉒ Date of filing: 24.11.88

㊿ Int. Cl.4: C 07 C 121/32
C 07 C 120/14, B 01 J 27/057

㉚ Priority: 25.11.87 JP 295054/87
18.02.88 JP 33999/88
09.08.88 JP 197126/88

㊸ Date of publication of application:
31.05.89 Bulletin 89/22

㊹ Designated Contracting States: DE FR GB IT NL

㉑ Applicant: MITSUBISHI KASEI CORPORATION
5-2, Marunouchi 2-chome Chiyoda-ku
Tokyo 100 (JP)

㉒ Inventor: Hatano, Masakatsu
2031-23 Kita-Hassaku-cho Midori-ku
Yokohama-shi Kanagawa-ken (JP)

Kayo, Atsushi
5-1, Tsutsujigaoka Midori-ku
Yokohama-shi Kanagawa-ken (JP)

㉔ Representative: Woods, Geoffrey Corlett et al
J.A. KEMP & CO. 14 South Square Gray's Inn
London WC1R 5EU (GB)

㊺ Process for producing nitriles.

㊼ A process for producing a nitrile which comprises subjecting an alkane and ammonia in the gaseous state to catalytic oxidation in the presence of a solid oxide catalyst comprising molybdenum, vanadium, tellurium and niobium.

EP 0 318 295 A1

D scription

PROCESS FOR PRODUCING NITRILES

The present invention relates to a process for pr ducing nitriles. More particularly, it relat s t an improved method for producing nitriles by using an alkane as starting material.

Nitriles such as acrylonitrile and methacrylonitrile have been industrially produced as an important intermediate for the preparation of fibers, synthetic resins, synthetic rubbers and the like. The most popular method for producing such nitriles is to subject an olefin such as propylene, isobutene or the like to a catalytic reaction with ammonia and oxygen in the presence of a catalyst in a gaseous phase at a high temperature.

More recently, there have been proposed methods for producing acrylonitrile or methacrylonitrile by using the so-called ammoxidation process, according to which a lower alkane such as propane, isobutane, etc., is subjected to a catalytic reaction with ammonia and oxygen in the presence of a catalyst in a gaseous phase. For instance, a method using an Mo type catalyst (Japanese Patent Application Laid-Open (KOKAI) Nos. 48-16887 (1973), 47-13312 (1972) (corresponding to GB 1,333,639), and 47-13313 (1972) (corresponding to USP 3,833,638) and Japanese Patent Publication No. 55-42071 (1980)), a method using V type catalyst (Jpn. Pat. Appln. Laid-Open (KOKAI) Nos. 47-33783 (1972) and 52-148022 (1977), Jpn. Pat. Pub. Nos. 50-23016 (1975) (corresponding to GB 1,336,135 and GB 1,336,136) and 47-51331 (1972) (corresponding to USP 3,433,823)), a method using Sb type catalyst (Jpn. Pat. Pub. Nos. 45-4733 (1970) (corresponding to GB 1,194,855), 47-14371 (1972) (corresponding to USP 3,670,008, USP 3,678,090 and USP 3,816,506), 50-17046 (1975) (corresponding to USP 3,670,006, USP 3,686,267 and USP 3,743,527), 50-28940 (1975) (corresponding to GB 1,334,859), 56-47901 (1981), and USP 3,686,295), and a method using other types of catalyst (Jpn. Pat. Pub. No. 50-16775 (1975) (corresponding to USP 3,652,638)) are known, but none of these known methods is satisfactory in selectivity of the objective nitriles.

In order to improve the selectivity of nitriles, it has been attempted to add a small quantity of an organic halide, inorganic halide or sulfur compound to the reaction system or to add water to the reaction system. However, the former method has a problem of possible corrosion of a reaction apparatus while the latter method involves a problem of formation of by-products by a side reaction.

Further, the methods using the conventional catalysts require a very high reaction temperature, which is about 500°C or higher, so that such methods are disadvantageous in terms of reactor material, production cost, etc.

The present inventors have made extensive researches on the method of producing nitriles by using an alkane as starting material and, as a result, found that by using a specific complex catalyst it was possible to produce the objective nitriles with a higher selectivity than attainable with the conventional methods, with no need of introducing a halide or water into the reaction system and at a lower temperature (about 380 to 480°C) than required in the conventional methods. The present invention was attained on the basis of such finding.

In an aspect of the present invention, there is provided a process for producing nitriles which comprises subjecting an alkane to a gas-phase catalytic oxidation reaction with ammonia in the presence of a complex oxide solid catalyst composed of molybdenum, vanadium, tellurium and niobium.

The feature of the present invention lies in using a complex oxide solid catalyst containing molybdenum (Mo), vanadium (V), tellurium (Te) and niobium (Nb) as essential components in the ammoxidation of alkane. Typical examples of such complex oxide solid catalyst are those represented by the following empirical formula:

$Mo_{1.0}V_aTe_bNb_cO_x$

wherein a, b and c represent atomic ratios of the respective component elements based on Mo, a being 0.01 to 1.0, b being 0.01 to 0.5 and c being 0.01 to 1.0, and x is a number decided by the total number of valencies of the metal elements.

These catalysts can be prepared in the following way for instance. Into an aqueous solution containing a given amount of ammonium metavanadate are added successively an aqueous solution of ammonium niobium oxalate, an aqueous solution of telluric acid and an aqueous solution of ammonium paramolybdate in such amounts that the atomic ratios of the respective metal elements would fall in the range specified above, and the mixture is heated and concentrated at about 70°C for about 30 minutes and then evaporated to dryness at 130°C. The resulting dry solid is calcined at a high temperature of from 350 to 650°C, preferably 350 to 450°C, for about 3 hours to give a desired catalyst.

In the above preparation process, the order of addition of the respective metal elements - molybdenum, vanadium, tellurium and niobium - is not specified, but it is desirable to add the molybdenum component, for example, an aqueous solution of ammonium paramolybdate, last of all as it faciliates obtaining a uniform aqueous solution.

In the above preparation, ammonium metavanadate may be replaced by V_2O_5, V_2O_3, $VOCl_3$, VCl_4 or the like. Ammonium niobium oxalate may be replaced by $NbCl_3$, $NbCl_5$, $Nb_2(C_2O_3)_5$ or the like. Also, telluric acid may be replaced by TeO_2 or the like, and ammonium paramolybdate may be replaced by MoO_3, $MoCl_5$, phosphomolybdic acid, silicomolybdic acid or the like. It is also possible to use a heteropolyacid which contains mixed-c odinat molybdenum and vanadium, such as molybdovanadophosphoric acid.

The contents of said metal elements constituting the catalyst used in the present invention are selected such that the ratio of vanadium to one atom of m lybdenum will be 0.01 to 1.0 atom, pr ferably 0.2 to 0.4 atom,

the ratio of tellurium to one atom of molybdenum will be 0.01 to 0.5 at m, preferably 0.2 to 0.4 atom, and the rati of niobium to one atom of molybdenum will be 0.01 to 1.0 atom, preferably 0.1 to 0.2 atom.

Such catalyst may be used eith r singly r in combination with a known carrier such as silica, alumina, aluminosilicat and th like. The catalyst is worked into a suitable particle diam ter and shape according to th scale and system of the reaction and/or other factors in the manner c mmonly practic d in th art.

The process of the present invention is a process for producing nitriles by subjecting alkanes t a gas-phase catalytic oxidation reaction with ammonia in the presence of th catalyst specified above.

As the alkane of the starting material, it is not particularly limited and for instance, alkanes of 1 to 7 carbon atoms such as methane, ethane, propane, butane, isobutane, pentane, hexane, heptane, etc. may be mentioned, however, in consideration of the industrial use of the nitrile to be produced, it is preferable to use a lower alkane of 1 to 4 carbon atoms. Further, the oxidation reaction of the process of the present invention is carried out by the oxygen atoms existing in the catalyst or by the molecular oxygen which is supplied with the starting material gas.

In the case where molecular oxygen is supplied with the starting material, although pure oxygen gas may be used, since the purity of oxygen gas is not required, it is economical to use a molecular oxygen-containing gas such as air. In the case where molecular oxygen is not contained in the supplied gas as the starting material, it is preferable to alternately supply a gaseous mixture of alkane and ammonia and a molecular oxygen-containing gas to prevent the reductive deterioration of the catalyst, or to transfer used catalysts continuously into an ordinary oxydative regenerator to use the thus regenerated catalyst while using reactor of moving bed type.

As the reactor used in the process according to the present invention, any one of the reactors hitherto used in a gas phase contact catalytic reaction may be used, and further, the introduction and the extraction of the catalyst may be carried out as in the conventional process. The catalyst is usually used in an amount of 0.02 to 2.4 cc, preferably 0.1 to 0.5 cc to one mole per hour of the supplied alkane.

Alkane, ammonia, the optional molecular oxygen-containing gas and a diluent gas optionally used for regulating the space velocity and the partial pressure of oxygen may be supplied individually to the reactor, however, it is preferable to mix these substances in advance and then to supply the thus prepared gaseous mixture to the reactor.

The amount of ammonia used in the reaction is 0.5 to 3 mol, preferably 0.8 to 1.5 mol per one mol of alkane.

The amount of the molecular oxygen-containing gas which is used in the case of necessity is important concerning the selectivity of the nitriles, and the molecular oxygen-containing gas is used so that the amount of molecular oxygen is not more than 5 mol, preferably 1 to 3 mol, more preferably 1 to 1.6 mol per one mol of alkane.

As the diluent gas, an inactive gas such as nitrogen, argon, helium, etc. may be used. By increasing and decreasing the amount used of the diluent gas in the above-mentioned range, it is possible to regulate the space velocity and the partial pressure of oxygen in the supplied gas into a suitable range.

The space velocity of the supplied gas (a mixture of alkane, ammonia, the molecular oxygen-containing gas optionally used and the diluent gas optionally used) is 100 to 10,000 hr^{-1}, preferably 500 to 2,000 hr^{-1}.

In the present invention, the gas phase contact reaction of alkane and ammonia is carried out at a temperature which is lower than the temperature of the conventional ammoxydation, namely 380 to 480°C, preferably 400 to 450°C under atmospheric pressure, a slightly increased pressure or a slightly reduced pressure.

In the case where the ammoxidation reaction of alkane is carried out according to the process of the present invention, for instance, an α,β-unsaturated nitrile such as methacrylonitrile, acrylonitrile, etc. is formed from isobutane and propane, acetonitrile is formed from ethane and hydrogen cyanide is formed from methane. In addition to these compounds, carbon monoxide, carbon dioxide, nitriles other than the objective nitrile, etc. are by-produced, however, the amount of production of the by-products is remarkably small.

Further, the separation of the objective nitrile from the reaction mixture,and the purification of the thus separated nitrile can be carried out while following the conventional method.

The present invention will be explained more in detail while referring to the following non-limitative Examples.

Further, the conversion (%) of an alkane and the selectivity(%) of a nitrile in Examples and Comparative Examples are respectively shown by the following formulae:

$$\text{Conversion of alkane(\%)} = \frac{\text{mols of consumed alkane}}{\text{mols of supplied alkane}} \times 100$$

$$\text{Selectivity of objective nitrile(\%)} = \frac{\text{mols of objective nitrile obtained}}{\text{mols of consumed alkane}} \times 100$$

REFERENCE EXAMPLE 1 (Preparation of the catalyst):

Into 100 ml of warm water, 1170 mg of ammonium metavanadate were dissolved, and into the thus formed solution, 12.5 ml of an aqueous solution of ammonium niobium oxalate (0.2 Nb atom/litre), 10.0 ml of an aqueous solution of telluric acid (0.5 Te atom/litre) and 25.0 ml of an aqueous solution of ammonium paramolybdate (1.0 Mo atom/liter) were added to prepare a uniform aqueous solution.

After heating the thus prepared aqueous solution, it was evaporated to dryness in a drier at 130°C to obtain a solid material.

The thus obtained solid material was calcined at 350° under a flow of air, and after molding the calcined material into a tablet of a size of 5 mm in diameter and 3 mm in length using a tablet machine, the tablet was pulverized and sifted into a powder of 16 to 28 mesh. The empirical formula of the thus prepared catalyst was as follows:

$Mo_{1.0}V_{0.4}Te_{0.2}Nb_{0.1}O_{4.65}$

REFERENCE EXAMPLE 2 (Preparation of the catalyst):

In the same manner as in Reference Example 1 except for changing the amount of telluric acid, the following two kinds of the catalyst were obtained:

$Mo_{1.0}V_{0.4}Te_{0.3}Nb_{0.1}O_{4.85}$ and

$Mo_{1.0}V_{0.4}Te_{0.4}Nb_{0.1}O_{5.05}$

EXAMPLES 1 to 4:

After charging a reactor with 0.5 cc of the catalyst obtained in Reference Example 1, a gaseous mixture of propane, ammonia, air and nitrogen in a molar ratio shown in Table 1 was supplied into the reactor at a space velocity of 1400 hr^{-1} to carry out the gas phase catalytic reaction at 422°C. The results are shown in Table 1.

TABLE 1

EXAMPLE	Composition of gas (molar ratio)				Conversion of propane (%)	Selectivity of acrylonitrile (%)
	Propane	NH_3	Air	N_2		
1	1	1.2	12.4	2.4	24.4	51.8
2	1	1.2	10.4	4.9	22.6	61.5
3	1	1.2	7.6	7.3	20.9	71.6
4	1	1.2	5.1	9.8	11.0	78.4

COMPARATIVE EXAMPLE 1:

While using a catalyst f the atomic ratl shown in Table 2 prepared in the same manner as in Reference Example 1 except for not using the Nb component, a gaseous mixture of propane, ammonia, air and nitrogen of the same composition as in Example 1 was supplied into a reactor at the same spac velocity as in Example 1 to carry out the reaction at the temperature shown in Table 2. The results are shown in Table 2.

COMPARATIVE EXAMPLE 2:

While using a catalyst of the atomic ratio shown in Table 2 prepared in the same manner as in Reference Example 1 except for not using the Te component, a gaseous mixture of propane, ammonia, air and nitrogen of the same composition as in Example 1 was supplied into a reactor at the same space velocity as in Example 1 to carry out the reaction at the temperature shown in Table 2. The results are shown in Table 2.

COMPARATIVE EXAMPLE 3:

While using a catalyst of the atomic ratio shown in Table 2 prepared in the same manner as in Reference Example 1 except for not using the V component, a gaseous mixture of propane, ammonia, air and nitrogen of the same composition as in Example 1 was supplied into the reactor at the same space velocity as in Example 1 to carry out the reaction at the temperature shown in Table 2. The results are shown in Table 2.

COMPARATIVE EXAMPLE 4:

While using a catalyst of the atomic ratio shown in Table 2 prepared in the same manner as in Reference Example 1 except for not using the Mo component, a gaseous mixture of propane, ammonia, air and nitrogen of the same composition as in Example 1 was supplied into a reactor at the same space velocity as in Example 1 to carry out the reaction at the temperature shown in Table 2. The results are shown in Table 2.

From the comparison of Examples 1 to 4 and Comparative Examples 1 to 4, it is understood that as the component of the catalyst of the present invention, all of Mo, V, Te and Nb are the indispensable components for obtaining a high selectivity.

TABLE 2

Comparative Example	Catalyst (atomic ratio)	Temperature (°C)	Conversion of propane (%)	Selectivity of acrylonitrile (%)
1	$Mo_{1.0}V_{0.4}Te_{0.2}O_{4.4}$	464	7.6	2.0
2	$Mo_{1.0}V_{0.4}Nb_{0.1}O_{4.25}$	417	34.2	10.5
3	$Mo_{1.0}Nb_{0.1}Te_{0.2}O_{3.65}$	423	0.3	trace
4	$V_{0.4}Nb_{0.1}Te_{0.2}O_{1.65}$	421	2.4	trace

EXAMPLE 5:

After charging a reactor with 1 cc of the catalyst btained in Reference Example 1, a gaseous mixture of propan , ammonia and nitrogen of the molar rati of 1:1.2:14.9 was supplied to the r act r at the space velocity of 700 hr-1 for 5 minutes to carry out the gas phase contact catalytic reacti n at 401°C.

The conversion was 9.9 % and the selectivity was 76.3 %.

Although in this Example, the oxidation reaction of propane was carried out without supplying molecular oxygen, acrylonitrile was obtained at a high selectivity only through oxidation reaction by the oxygen atoms which existed in the catalyst.

EXAMPLES 6 and 7:

While respectively using 0.5 cc of each of the two catalysts obtained in Reference Example 2 and supplying the gaseous mixture of propane, ammonia, air and nitrogen of the molar ratio of 1:1.2:7.6:7.3 at the space velocity of 1400 hr^{-1} to a reactor, the gas phase contact catalytic reaction was carried out at 422°C.

The results are shown in Table 3.

TABLE 3

Example	Catalyst (atomic ratio)	Temperature (°C)	Conversion of propane (%)	Selectivity of acrylonitrile (%)
6	$Mo_{1.0}V_{0.4}Te_{0.3}Nb_{0.1}O_{4.85}$	423	20.2	60.9
7	$Mo_{1.0}V_{0.4}Te_{0.4}Nb_{0.1}O_{5.06}$	424	15.2	52.7

EXAMPLES 8 to 10:

After charging a reactor with 0.5 cc of the catalyst obtained in Referenc Example 1, the gaseous mixture f isobutane, amm nia, air and nitrog n f a c mposition shown in Tabl 4 was suppli d t the reactor at a spac velocity of 1400 hr^{-1} t carry out the gas phase contact catalytic reaction at 448°C. The results ar sh wn in Table 4.

TABLE 4

EXAMPLE	Composition of gas (molar ratio)				Conversion of isobutane (%)	Selectivity of methacrylonitrile (%)
	Isobutane	NH_3	Air	N_2		
8	1	1.2	7.6	7.3	15.2	22.4
9	1	1.2	5.1	9.8	11.0	42.7
10	1	1.2	2.7	12.2	6.0	41.6

Claims

1. A process for producing a nitrile which comprises subjecting an alkane and ammonia in the gaseous state to catalytic oxidation in the presence of a solid oxide catalyst comprising molybdenum, vanadium, tellurium and niobium.

2. A process according to claim 1 wherein the catalyst has the empirical formula: $Mo_{1.0}V_aTe_bNb_cO_x$ wherein a is from 0.01 to 1.0, b is from 0.01 to 0.5, c is from 0.01 to 1.0 and x represents a number such that the total valency of the metal elements is satisfied.

3. A process according to claim 2 wherein a is from 0.2 to 0.4, b is F.rom 0.2 to 0.4 and c is from 0.1 to 0.2.

4. A process according to any one of the previous claims which is carried out in the presence of molecular oxygen.

5. A process according to any one of the preceding claims wherein the alkane contains from 1 to 4 carbon atoms.

6. A process according to any one of the preceding claims wherein the catalyst is present in an amount of from 0.02 to 2.4 cm^3 per 1 mole per hour of the alkane.

7. A process according to any one of the preceding claims wherein the ammonia is present in an amount of from 0.5 to 3 mol per 1 mol of alkane.

8. A process according to any one of the preceding claims which is carried out at a temperature of from 380 to 480° C.

9. A catalyst as defined in claim 2 or 3.

10. A process for producing a catalyst as defined in claim 9 which comprises adding to an aqueous solution of ammonium metavanadate, V_2O_5, V_2O_3, $VOCl_3$ or VCl_4, in any order:

i) an aqueous solution of ammonium niobium oxalate, $NbCl_3$, $NbCl_5$ or $Nb_2(C_2O_4)_5$:

ii) an aqueous solution of telluric acid or TeO_2; and

iii) an aqueous solution of ammonium paramolybdate, MoO_3, $MoCl_5$, phosphomolybdic acid, silicomolybdic acid or a heteropoly acid which contains mixed-coordinate molybdenum and vanadium, subsequently heating the mixture, concentrating the mixture to dryness and calcining the resulting dry solid.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 31 1148

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A-2 173 203 (ASAHI GLASS) * Claims 6,7; exemples 86,114,115 *	9,10	C 07 C 121/32 C 07 C 120/14 B 01 J 27/057
A	GB-A-2 090 156 (MONSANTO) * Exemple 19 *	1-8	
A	GB-A-1 334 859 (ICI) * Claims; exemples 7,8 *	1-8	
D,A	US-A-3 833 638 (W.R. KNOX) * Exemple II; tables A,B *	1-8	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

B 01 J 27/00
C 07 C 120/00
C 07 C 121/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-02-1989	WRIGHT M.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document